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Procedia Chemistry 19 (2016) 906 – 909

Procedia Chemistry

5th International Conference on Recent Advances in Materials, Minerals and Environment (RAMM) & 2nd International Postgraduate Conference on Materials, Mineral and Polymer (MAMIP), 4-6 August 2015

Investigation of the Mixing Medium Effect on the Development of the CCTO Microstructure at 1000 ^{o}C

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Abstract

In this work, CCTO ceramics with high permittivity were synthesize using solid state reaction. The raw materials such as CuO, CaO and TiO_2 were prepared in dry medium and wet medium (deionized water, distilled water and ethanol) and calcined at 1000^{o}C for 5h. From this study, mixing medium effect on CCTO microstructure and it can control the growth of CCTO. This part is significant for the progress of CCTO. Particle size of CCTO prepared using dry medium is homogenous and largest compare to CCTO prepared using wet medium. This is relate to conversion rate and the existence of pore inside CaO and empty space between particles.

Peer-review under responsibility of School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia

Keywords: CCTO, mixing medium, microstructure

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Peer-review under responsibility of School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia
doi:10.1016/j.proche.2016.03.133

1. Introduction

Interest in the ceramic with giant permittivity (ε') has been paid very fast in microelectronic technology beyond its theoretical aspects. One of the drawback is that most of giant permittivity ceramic exhibited ferroelectric-like, which shown strong temperature dependence. Hence, a new material with outstanding dielectric properties and good stability as respect to the frequency and the temperature has to be developed in order to overcome this problem.

Current study report that dielectric constant of $CaCu_3Ti_4O_{12}$ (CCTO) ceramic is ~10^5 at room temperature and the temperature independence between 1000 and 600 K[1,2]. The dielectric response almost constant in a range of frequencies 20 Hz to 10^6 Hz. These properties have make CCTO a highly potential candidate used in microelectronic applications such as capacitors and memory devices. In spite the origin of giant permittivity CCTO has still remain unclear, it is now widely accepted that the high dielectric response is associated with extrinsic effects. The reason for CCTO's high permittivity is believed as effect from the formation of multi-conductive layers between semiconducting grain and insulating grain boundary, very similar to the internal barrier layer capacitor (IBLC) model[3].

The high permittivity of these IBLC materials are directly correlated with microstructure, as they are sensitive to processing[3]. It is well known that two heating processes, i.e. calcination and sintering[4] play significant roles in controlling the final properties of the microstructure. The effect of the heating process, i.e. temperature[3,4] and time[4,5,6] have been intensively investigated, which indicate that the calcination process has primary effect in controlling microstructure properties of CCTO. CuO is normally found in the calcination process of CCTO, which believed its act as densification agent and abnormal grain growth of CCTO. As the results, the final sintered CCTO is exhibited electronically heterogeneous, which devoted big problematic for reproducibility and reliability of dielectric permittivity. Meanwhile, some reports explained that there is few microstructure changes when sintered from pure CCTO powders[7,8], which indicate that the abnormal grain growth in CCTO could be controlled.

Instead of calcination, mixing process also has been found as one of the important parameter need to be considered in the preparation of CCTO. Inadequate mixing process could contribute to the poor homogeneity of powders, thus lowering the purity of CCTO in the calcination process. Studies have attempted to investigate the effect of calcination and sintering processes, where the powders were mixed with various mixing medium. In this work, the investigation on the effect of mixing condition (dry and wet) on the particle size variation of CCTO ceramic was conducted and reported in this paper. The result is very important for the development of CCTO with controllable microstructure features.

2. Experimental Details

$CaCu_3Ti_4O_{12}$ precursor in this study was prepared by conventional solid state method. Commercial powders of CaO ($d_{50} \approx$ 5.25 µm, 99.9 % purity), CuO ($d_{50} \approx$ 10.24 µm, 99.9% purity) and TiO_2 ($d_{50} \approx$ 9.32 µm, 99.9 % purity) were used as raw material. The raw materials were weighted according to the stoichiometry ratio of CCTO (CaO: CuO: TiO_2 = 1: 3:4) and added with zirconia balls (weight ratio of mixture to ball is 10:1) into of 500 ml polyethylene (Super 90) bottle. Then the raw materials prepared using dissimilar mixing medium: dry mixing and wet mixing. For dry mixing, the sample was labelled as DM and wet mixing as WM. There are three wet mediums such as deionized water, distilled water and ethanol and labelled as WM_Deionized, WM_Distilled and WM_Ethanol respectively. All mixtures were mixed using a rotary ball mill (Heidolph Overhead Shaker Reax 2) at 120 rpm for 24 h then dried overnight in the oven (Memmert UM 400) at 100 °C. The resulting product was calcined in air at 1000 °C for 5 h. Phase structure of calcined powders was characterized using X-ray diffraction (Bruker AXS D8 Advance) with Cu-Kα1 radiation at scan speed of 0.2 °/s. The phase composition of XRD profiles was characterized using PANalytical X'Pert Highscore Plus software.

3. Results and Discussion

Fig. 1. shows an example of XRD patterns for calcined CCTO powder at 1000 °C for 5 h, which was prepared with different mixing medium. All XRD patterns could be indexed to the ICSD file number of 98-005-8087, with body-centered cubic perovskite-related structure under the space group of Im3. The lattice parameter (a) of all samples is relatively similar to each other, ~7.391 nm. From the observation, no secondary phases could be detected. The major peaks in the figure is correspond to (211), (220), (013), (222), (321), (400), (422), (440), and (620). The structure arrangement is body-centered cubic (bcc) and lattice parameter is 7.391 nm.

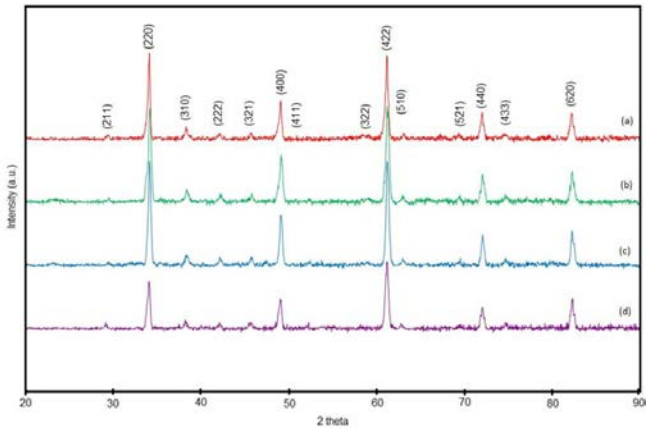

Fig. 1. XRD pattern of CCTO powder mixture for various mixing mediums after firing at 1000 ^{o}C for 5 h: (a) deionized water (b) distilled water, (c) ethanol and (d) dry medium

Figure 2 shows FESEM images of CCTO as prepared with different mixing medium. All samples calcined at 1000 ^{o}C for 5 hrs. From the images, CCTO as prepared with DM exhibited unimodal size distribution, ~5 µm. However, the other samples showed bimodal size distribution in the range of 0.1 – 1 µm. Various grain size may effected by mixing medium.

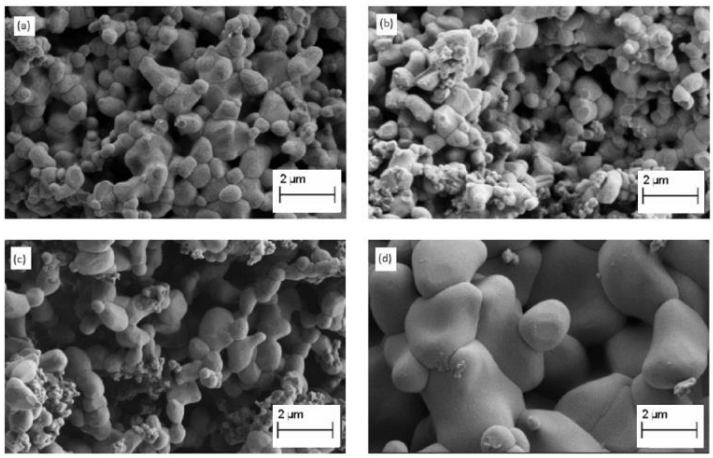

Fig. 2: FESEM micrograph of CCTO powder with various mixing media (a) deionized water (b) distilled water, (c) ethanol and (d) dry media fired at 1000 ^{o}C, respectively.

During the mixing process, there are conversion rate of CCTO from reactant and it was changed during the process. CaO is exothermically react with water [$CaO + H_2O \rightarrow Ca(OH)_2$] and in also react with ethanol [$CaO + 2C_2H_6O \rightarrow Ca(OH)_2 + (C_2H_5)_2O$]. The conversion rate of CaO into $Ca(OH)_2$ is lowest in DM while in water e.g. WM_deionized and WM_distilled, the rate is highest. During the calcination process, hydroxide will evaporated and create pore inside CaO. The pore will restrict the grain growth of CCTO. For CCTO prepared in DM, the pore inside CaO is low compare to CCTO prepared in WM_deionized and WM_distilled. This is agree with FESEM result that shows the grain size of CCTO prepared in DM is largest compare to other sample because of the existence of pore. For sample prepare in ethanol, ethyl also will evaporated and create pore and leave the empty space among particles. The empty space between particles and pore inside CaO will limit the growth of CCTO as shown in Figure 2. This result may affect the dielectric properties of CCTO and CCTO prepared using DM may have higher dielectric constant compare to other medium due to largest grain size.

4. Conclusion

In summary, single phase of CCTO ceramics produced by conventional solid state reaction and had be confirmed on structure through XRD. All samples prepared using dry and wet medium. Different mixing media gave effect on CCTO microstructure when the samples calcined at 1000^{o}C. Morphology from FESEM shows that sample prepared using dry medium shows the largest grain and exhibit unimodal size distribution compare to others. These finding is because of the pores inside CaO and empty space between particles.

Acknowledgements

This work was supported by the Fundamental Research Grant Scheme of Malaysia (FRGS) under grant no. 203/PBAHAN/6071263

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